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ARPES study of Fe_xTiS_2 ($x = 0 \leq x \leq 0.33$)

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$1T$-TiS$_2$ is non-magnetic layered material with $1T$-CdI$_2$-type crystal structure. The hexagonal layer of Ti ions is sandwiched between the two hexagonal layers of S ions and the Ti ion is octahedrally coordinated with six S ions. The S-Ti-S triple layers are covalently bonded and these TiS$_2$ triple layers are weakly coupled with van der Waals (vdW) force. In the vdW gap located between the TiS$_2$ layers, the other $3d$ transition-metal M can be intercalated as M_xTiS_2. Among them, Fe_xTiS_2 exhibits a wide variety of magnetic properties [1]. With increasing the Fe concentration from $x = 0$, the cluster spin grass (CG) state with the Ising spins is found for $x < 0.20$. After exhibiting the antiferromagnetic (AFM) state from $x = 0.20$ to 0.28, the CG state is again realized for $0.28 < x < 0.38$ and the AFM state for $0.38 < x < 0.50$. Above $x = 0.50$, the ferrimagnetic behavior is observed. On the other hand, the Fe ion intercalated in the vdW gap between the TiS$_2$ layers occupy the octahedral site surrounded by six S ions. X-ray studies reveal the Fe random distribution for $x < 0.20$, while the formation of $2\sqrt{3}a \times 2a \times 2c$ superlattices due to the Fe ordering for $x = 0.25$ and $\sqrt{3}a \times \sqrt{3}a \times 2c$ superlattice for $x = 0.33$. The rich magnetic states of Fe_xTiS_2 are expected to link to the change in electronic band structure due to the Fe intercalation. In this study, we carried out angle-resolved photoemission spectroscopy (ARPES) to reveal the electronic band structure of Fe_xTiS_2 ($0 \leq x \leq 0.33$) at beamlines BL-1, BL-7 and BL-9A of Hiroshima Research Institute for Synchrotron Radiation Science (HiSOR).

Figures 1(a), (b) and (c) shows the ARPES intensity plots of TiS$_2$, Fe$_{0.25}$TiS$_2$ and Fe$_{0.33}$TiS$_2$, respectively, measured at hv=66 eV along the $\bar{\Gamma}$-$\bar{M}$ directions of the surface Brillouin zone, roughly corresponding to Γ-M direction of the bulk Brillouin zone, estimated from the hv-dependent measurements. The ARPES spectra were taken at 20 K and with p-polarized geometry. For TiS$_2$ in Fig. 1(a), we find an electron pocket derived from the Ti $3d$ states around the M point, which is resonantly enhanced in intensity around the Ti $3p$-$3d$ absorption region. Almost non-dispersive band is observed just below the electron pocket, which is assigned to the localized $3d$ states of the Ti ions self-intercalated in the vdW gap between TiS$_2$ layers. The electron pocket is hardly observed in the ARPES spectra with s-polarized geometry (not shown here), suggesting that it comes from the Ti $3d_{z^2}$ component. The parabolic band around the Γ point is due to the S $3p$ states.

The electron pocket around the M point is shifted to higher binding energy on going from TiS$_2$ (Fig. 1(a)) to Fe$_{0.25}$TiS$_2$ (Fig. 1(b)) and further to Fe$_{0.33}$TiS$_2$ (Fig. 1(c)) and as the results it becomes large. In addition, the parabolic S $3p$ band also becomes deeper with increasing the Fe concentration. These results indicate that electrons are transferred from the intercalated Fe ions to host TiS$_2$ layers. The dispersive Fe $3d$-derived band is observed around $E_B = 0.4$ eV for Fe$_{0.25}$TiS$_2$ and Fe$_{0.33}$TiS$_2$ as shown by dashed lines in Figs. 1(b) and 1(c), reflecting the Fe ions align periodically in the vdW gap parallel to the TiS$_2$ layers (in plane). The periodicity of the Fe $3d$ band for Fe$_{0.25}$TiS$_2$ becomes half of that of $\bar{\Gamma}$-$\bar{M}$-$\bar{\Gamma}$ for TiS$_2$, reflecting the $2\sqrt{3}a \times 2a$ periodicity in plane for $x = 0.25$. The periodicity of the Fe $3d$ band becomes long for Fe$_{0.33}$TiS$_2$, which is qualitatively understood from the shorter $\sqrt{3}a \times \sqrt{3}a$ periodicity in plane for $x = 0.33$. In addition, the Fe $3d$ band is more dispersive for Fe$_{0.33}$TiS$_2$. On the other hand, the Fe $3d$ band is almost flat for Fe$_{0.10}$TiS$_2$ and

$Fe_{0.15}TiS_2$, indicating that the Fe $3d$ states almost localized due to the random distribution of the Fe ions.

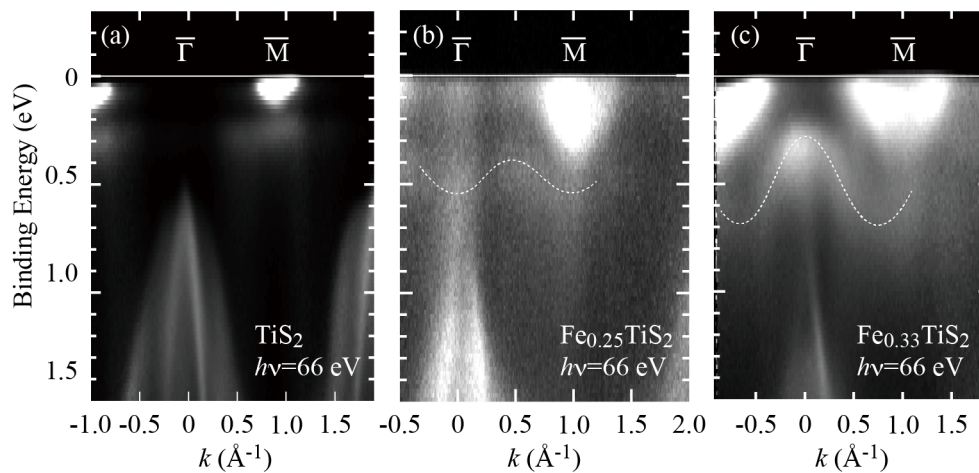**FIGURE 1.** ARPES intensity plots of (a) TiS_2, (b) $Fe_{0.25}TiS_2$ and (c) $Fe_{0.33}TiS_2$ measured at $h\nu = 66$ eV along $\bar{\Gamma}$-$\bar{M}$ direction. Dashed lines in (b) and (c) are guide for the eye for the Fe $3d$ band.

We measured the ARPES spectra of TiS_2, $Fe_{0.25}TiS_2$ and $Fe_{0.33}TiS_2$ along the Γ-A direction with changing $h\nu$ from 30 to 124 eV at 20 K with p-polarized geometry. We find that the Fe $3d$ bands for $Fe_{0.25}TiS_2$ and $Fe_{0.33}TiS_2$ exhibit the dispersion along the direction normal to the TiS_2 layers and has half period of the S $3p$ band, reflecting the $2c$ periodicity for $x = 0.25$ and 0.33.

REFERENCES

1. N. V. Selezneva, E. M. Sherokalova, A. Podlesnyak, M. Frontzek and N. V. Baranov, Phys. Rev. Mater. **7**, 014401 (2023).